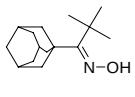
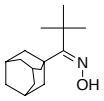
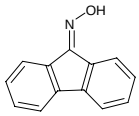
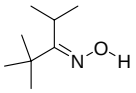
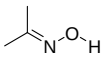
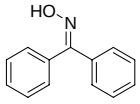
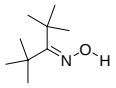
O-H Bond Dissociation Enthalpies in Oximes: A Theoretical Assessment and Experimental Implication

Sha-Sha Chong, Yao Fu, Lei Liu, Qing-Xiang Guo

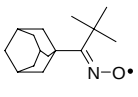
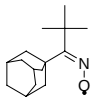
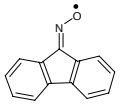
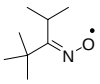
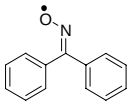
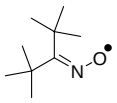
Supporting Information

Table S1 Calculated single-point energies of benchmark molecules (Unit: Hartree)[a]

							
ZPE	0.383998	0.384136	0.186552	0.244452	0.101178	0.207894	0.272278
TCE	0.400421	0.400578	0.198257	0.257756	0.108491	0.220957	0.286936
Hcorr	0.385061	0.385213	0.190795	0.247978	0.104444	0.212641	0.276045
b3lyp	-716.81095	-716.81048	-630.94083	-445.16773	-248.55099	-632.13552	-484.48161
b3p86	-719.18135	-719.18083	-632.76389	-446.61479	-249.26567	-633.99292	-486.07581
b3pw91	-716.54700	-716.54648	-630.68671	-444.99445	-248.45105	-631.87753	-484.29379
bmk	-716.32250	-716.32216	-630.52005	-444.85242	-248.38570	-631.70369	-484.13707
mpw1kcis	-716.34319	-716.34264	-630.59163	-444.86718	-248.40167	-631.77046	-484.15084
mpwpw91	-716.68834	-716.68780	-630.86533	-445.08464	-248.51507	-632.04989	-484.38973
pbe1pbe	-715.95898	-715.95845	-630.19964	-444.62314	-248.25364	-631.38162	-483.88819
bhandh	-711.36858	-711.36797	-626.32199	-441.79601	-246.76886	-627.46757	-480.79439
bhandhlyp	-716.35218	-716.35174	-630.55269	-444.87219	-248.39004	-631.74091	-484.15896
mpw1b95	-716.42590	-716.42570	-630.65294	-444.90870	-248.41792	-631.83102	-484.19776
mpw1k	-716.63513	-716.63464	-630.73411	-445.03420	-248.45984	-631.92478	-484.33982

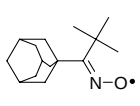
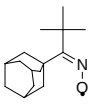
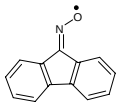
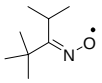
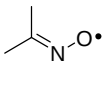
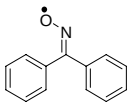
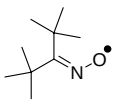
[a]The zero-point energy (ZPEs) and thermal corrections to enthalpies (TCEs) were obtained at the (U)B3LYP/6-31G(d) level. A scaling factor (0.96) for ZPEs is applied in consistency with the ONIOM-G3B3 requirement. The actual thermal corrections added to single-point energies are calculated as Hcorr = TCE – ZPE + 0.96 ZPE

Table S2 Calculated single-point energies of benchmark radicals using UDFTs (Unit: Hartree)[a]

								H
ZPE	0.371611	0.371757	0.174134	0.231938	0.089004	0.195856	0.260011	0.000000
TCE	0.387816	0.387983	0.185611	0.245099	0.096054	0.208561	0.274378	0.002360
Hcorr	0.372952	0.373113	0.178646	0.235821	0.092494	0.200727	0.263978	0.002360
b3lyp	-716.18430	-716.18441	-630.30685	-444.53404	-247.91260	-631.50224	-483.85419	-0.50226
b3p86	-718.53457	-718.53468	-632.10991	-445.96079	-248.60721	-633.33973	-485.42826	-0.51857
b3pw91	-715.92117	-715.92128	-630.05372	-444.36145	-247.81346	-631.24495	-483.6672	-0.50407
bmk	-715.69467	-715.69486	-629.88360	-444.21701	-247.74547	-631.06864	-483.50826	-0.49863
mpw1kcis	-715.72357	-715.72369	-629.96489	-444.24041	-247.77009	-631.14401	-483.53047	-0.50679
mpwpw91	-716.06863	-716.06889	-630.23914	-444.45792	-247.88363	-631.42401	-483.76930	-0.50307
pbe1pbe	-715.33613	-715.33622	-629.56955	-443.99304	-247.61909	-630.75219	-483.26455	-0.50115
bhandh	-710.75504	-710.75506	-625.70073	-441.17479	-246.14382	-626.84823	-480.17998	-0.47798
bhandhlyp	-715.72552	-715.72558	-629.91811	-444.23836	-247.75184	-631.10730	-483.53147	-0.49860
mpw1b95	-715.80347	-715.80356	-630.02292	-444.27872	-247.78351	-631.20179	-483.57458	-0.49753
mpw1k	-716.00606	-716.00613	-630.09742	-444.39781	-247.81916	-631.28875	-483.70994	-0.50433

[a]The zero-point energy (ZPEs) and thermal corrections to enthalpies (TCEs) were obtained at the (U)B3LYP/6-31G(d) level. A scaling factor (0.96) for ZPEs is applied in consistency with the ONIOM-G3B3 requirement. The actual thermal corrections added to single-point energies are calculated as Hcorr = TCE – ZPE + 0.96 ZPE

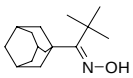
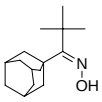
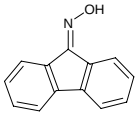
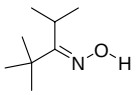
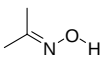
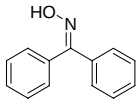
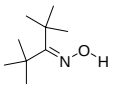
Table S3 Calculated single-point energies of benchmark radicals using RODFTs (Unit: Hartree)[a]

								H
ZPE	0.371611	0.371757	0.174134	0.231938	0.089004	0.195856	0.260011	0.000000
TCE	0.387816	0.387983	0.185611	0.245099	0.096054	0.208561	0.274378	0.002360
Hcorr	0.372952	0.373113	0.178646	0.235821	0.092494	0.200727	0.263978	0.002360
b3lyp	-716.18215	-716.18226	-630.30456	-444.53188	-247.91044	-631.49999	-483.85203	-0.50226
b3p86	-718.53248	-718.53261	-632.10770	-445.95871	-248.60512	-633.33756	-485.42617	-0.51857
b3pw91	-715.91899	-715.91911	-630.05140	-444.35927	-247.81129	-631.24268	-483.66502	-0.50407
bmk	-715.69241	-715.69259	-629.88119	-444.21475	-247.74324	-631.06629	-483.50599	-0.49863
mpw1kcis	-715.72187	-715.72199	-629.96307	-444.23871	-247.76838	-631.14223	-483.52877	-0.50679
mpwpw91	-716.06739	-716.06766	—[b]	-444.45667	-247.88236	-631.42270	-483.76805	-0.50307
pbe1pbe	-715.33363	-715.33372	-629.56688	-443.99054	-247.61659	-630.74957	-483.26204	-0.50115
bhandh	-710.75101	-710.75103	-625.69629	-441.17078	-246.13986	-626.84396	-480.17595	-0.47798
bhandhlyp	-715.72103	-715.72109	-629.91322	-444.23390	-247.74743	-631.10256	-483.52699	-0.49860
mpw1b95	-715.80114	-715.80152	-630.02060	-444.27641	-247.78116	-631.19937	-483.57230	-0.49753
mpw1k	-716.00219	-716.00226	-630.09322	-444.39396	-247.81534	-631.28467	-483.70607	-0.50432

[a]The zero-point energy (ZPEs) and thermal corrections to enthalpies (TCEs) were obtained at the (U)B3LYP/6-31G(d) level. A scaling factor (0.96) for ZPEs is applied in consistency with the ONIOM-G3B3 requirement. The actual thermal corrections added to single-point energies are calculated as Hcorr = TCE – ZPE + 0.96 ZPE

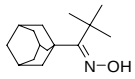
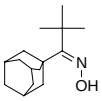
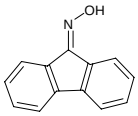
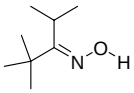
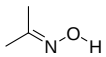
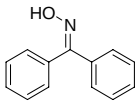
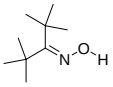
[b]ROmPWPW91 functional fails to reach a SCF convergence.

Table S4 Calculated O-H bond dissociation enthalpies using UDFTs (Unit: kcal/mol)

							
Exp[1].	77.0	76.5	82.0	82.6	84.3	82.4	79.0[a]
b3lyp	71.9	71.6	76.5	76.3	79.4	76.2	72.5
b3p86	74.3	73.9	78.8	78.8	81.8	78.5	74.8
b3pw91	70.3	69.9	74.8	74.8	77.8	74.6	70.8
bmk	75.0	74.6	80.3	79.7	82.8	79.6	75.6
mpw1kcis	64.7	64.3	69.1	69.1	72.3	69.1	65.2
mpwpw91	67.1	66.6	71.1	71.4	74.5	71.1	67.6
pbe1pbe	70.3	69.9	74.8	74.8	77.7	74.5	70.8
bhandh	78.9	78.6	83.8	83.7	86.3	82.7	79.5
bhandhlyp	74.2	73.9	79.2	78.7	81.6	78.7	74.8
mpw1b95	72.3	72.1	77.0	77.0	79.9	76.6	72.8
mpw1k	72.2	71.8	76.9	76.7	79.5	76.6	72.7

[a] The arithmetic average of the revised calorimetric value(79.2kcal/mol) and the O-H BDE derived from the measured rates of thermolysis of *O*-benzyl oxime ether(78.8kcal/mol) is taken.

Table S5 Calculated O-H bond dissociation enthalpies using RODFTs (Unit: kcal/mol)

							
Exp[1].	77.0	76.5	82.0	82.6	84.3	82.4	79.0[b]
b3lyp	73.3	72.9	77.9	77.7	80.8	77.6	73.8
b3p86	75.6	75.2	80.2	80.1	83.1	79.8	76.2
b3pw91	71.7	71.3	76.2	76.1	79.1	76.1	72.2
bmk	76.4	76.1	81.8	81.1	84.2	81.1	77.0
mpw1kcis	65.8	65.3	70.3	70.2	73.4	70.2	66.2
mpwpw91	67.9	67.3	–[a]	72.2	75.3	71.9	68.3
pbe1pbe	71.8	71.4	76.4	76.3	79.3	76.1	72.3
bhandh	81.5	81.1	86.6	86.3	88.8	85.4	82.1
bhandhlyp	77.1	76.8	82.3	81.5	84.3	81.7	77.6
mpw1b95	73.7	73.4	78.4	78.4	81.3	78.2	74.2
mpw1k	74.6	74.2	79.6	79.1	81.9	79.2	75.1

[a] ROmPWPW91 functional fails to reach a SCF convergence for the single point energy calculation of the fluorenone iminoxy radical.

[b] The arithmetic average of the revised calorimetric value(79.2kcal/mol) and the O-H BDE derived from the measured rates of thermolysis of *O*-benzyl oxime ether(78.8kcal/mol) is taken.

References and Notes:

(1) Pratt, D. A.; Blake, J. A.; Mulder, P.; Walton, J. C.; Korth, H. G.; Ingold, K. U. *J. Am. Chem, Soc* **2004**, *126*, 10667.